



Hydrogen production on molybdenum in H₂SO₄ solutions



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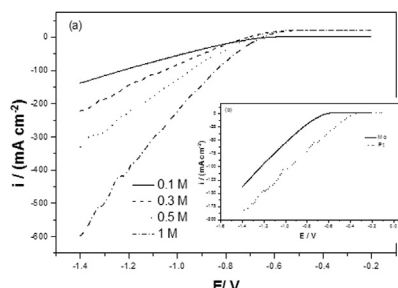
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HIGHLIGHTS

- Mo electrode was used for hydrogen production in acid solution.
- 0.1–1.0 M H₂SO₄ solution is a suitable electrolyte.
- The electrode was used for 7 days without any deterioration.
- The rate of hydrogen evolution did not change with prolonged use.
- The activation energy of the HER in 0.1 M H₂SO₄ is $\approx 13 \text{ kJ mol}^{-1}$ at -1.2 V .

GRAPHICAL ABSTRACT



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ABSTRACT

Molybdenum was used as cathode for the hydrogen production from acid solutions. The effect of acid concentration, cathodic potential and temperature on the rate of hydrogen evolution was investigated and discussed. The results were compared with those of platinum. Open circuit potential measurements, polarization technique and EIS were used. Impedance measurements under open circuit conditions and under cathodic polarization were carried out and the data were fitted to theoretical data according to a proposed electronic circuit model. The results reveal that molybdenum is a good candidate for hydrogen production for long time. The rate of hydrogen evolution is constant and no electrode deterioration was noticed. The process is economic and convenient and does not need any special treatments.

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1. Introduction

One way of stabilizing the energy supply is to use different energy carriers. Hydrogen can be considered as one of the environmentally safe energy carriers that could be used anywhere when there is a lack of energy [1]. It can be produced easily by water electrolysis and made into power, heat and water in fuel cells. The electrochemical reactions in fuel cells are always catalyzed and the

catalysts used are usually based on platinum or platinum/ruthenium alloys, which are both scarce and expensive. The use of efficient catalysts for hydrogen evolution, which are based on cheap and abundant materials, is the main task of different research groups. It is therefore important to find alternatives to the Pt group catalysts or to find materials that do not need such catalysts.

The hydrogen evolution reaction, HER, was attracting many researchers from the last century and the work of Bockris et al. had encouraged many authors to study the HER on different materials [2]. In the last decades and due to the energy crisis, the HER was extensively studied on metals, alloys and oxides [3–9]. The extensive investigations carried out on molybdenum disulfide composite cathodes have led to their use for hydrogen evolution.

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An electrochemical performance superior to stainless steel or Pt-based cathodes in phosphate or perchlorate electrolytes was reported [10]. The hydrogen evolution reaction on electrodeposited Ni-Mo alloy coatings was studied and the electrochemical properties of these alloys were investigated by polarization measurements, cyclic voltammetry and EIS technique [11,12]. It was reported that the electrodeposited Ni-Mo alloy coatings possess remarkably high catalytic activity for hydrogen evolution; they exhibited porous surface morphology and much better activity toward the HER than pure Ni electrodes. Very recently, a nano Ni-Co film cathode was used successfully for the hydrogen evolution. The electrode was applied continuously for weeks with remarkably constant hydrogen evolution rate without any special treatment [13]. Mo itself is interesting since it can serve as a promising cathode for the HER [2]. It was considered as good candidate for the cathodic hydrogen evolution from basic solutions on a large scale and for a long time without deterioration [14].

Molybdenum is an important valve metal that is frequently used as alloying element with iron and steels to facilitate the

formation of passive films and to improve pitting corrosion resistance [15]. The passive film formed on Mo, especially in basic or neutral solutions, consists mainly of MoO_2 [16,17]. In acidic solutions MoO_3 was also identified as a constituent of the passive film beside MoO_2 . In aqueous solutions of different pH and in the presence of chloride or sulfate anions the passive film consists mainly of Mo_2O_5 layers [18]. The stability of the passive film on Mo was found to depend on the solution pH and the soluble product is molybdate or molybdic acid [18,19]. It was reported that the anodization of Mo at potentials above 5 V in H_2SO_4 or H_3PO_4 produces highly stable barrier films on the metal surface [20]. The investigations concerning the cathodic hydrogen evolution were based on the analysis of the Tafel parameters obtained from the electrochemical measurements and the variations of potentials with different experimental parameters like temperature or pH [21,22]. Most electrode materials may change Tafel slopes at similar potentials depending on the surface hydrogen coverage [5,23]. It is important to use different techniques to obtain detailed information about the kinetics and mechanism of

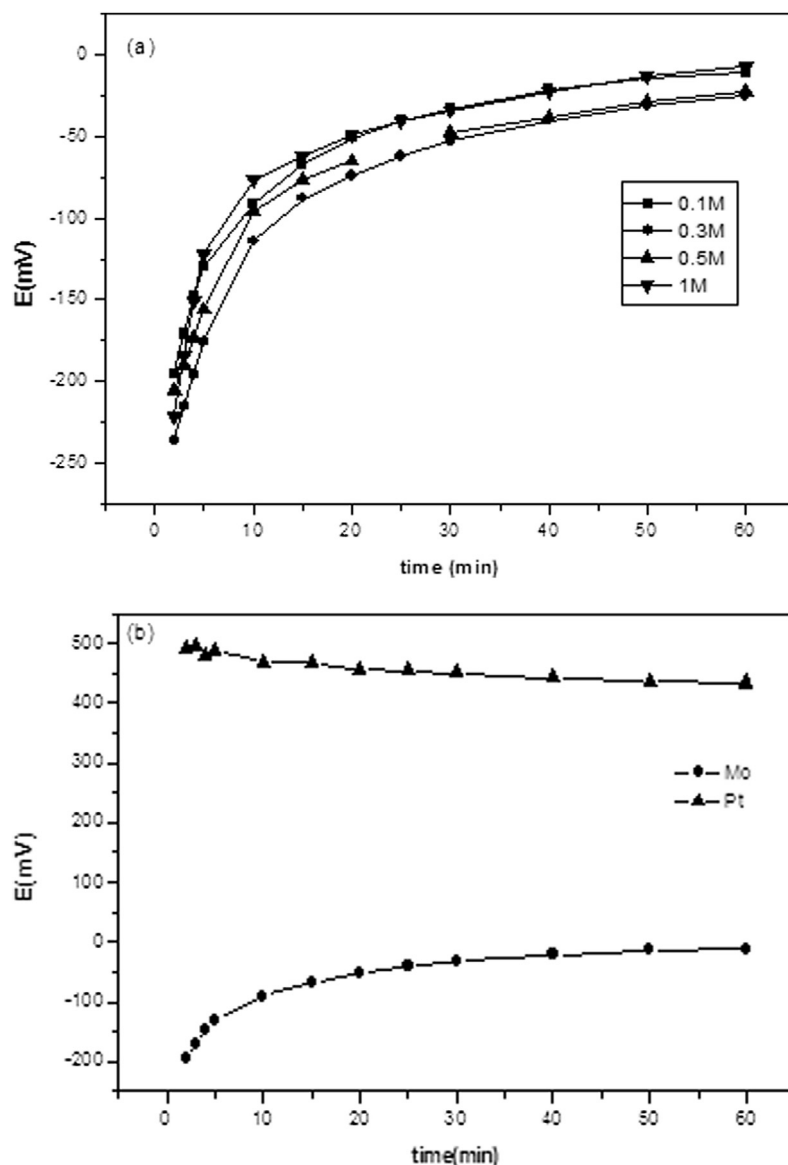


Fig. 1. a) Variation of the open circuit potential with time for Mo electrode immersed in H_2SO_4 solutions of different concentrations at 25 °C. b) Variation of the open-circuit potential with time for Mo and Pt electrodes in stagnant naturally aerated 0.5 M H_2SO_4 solution.

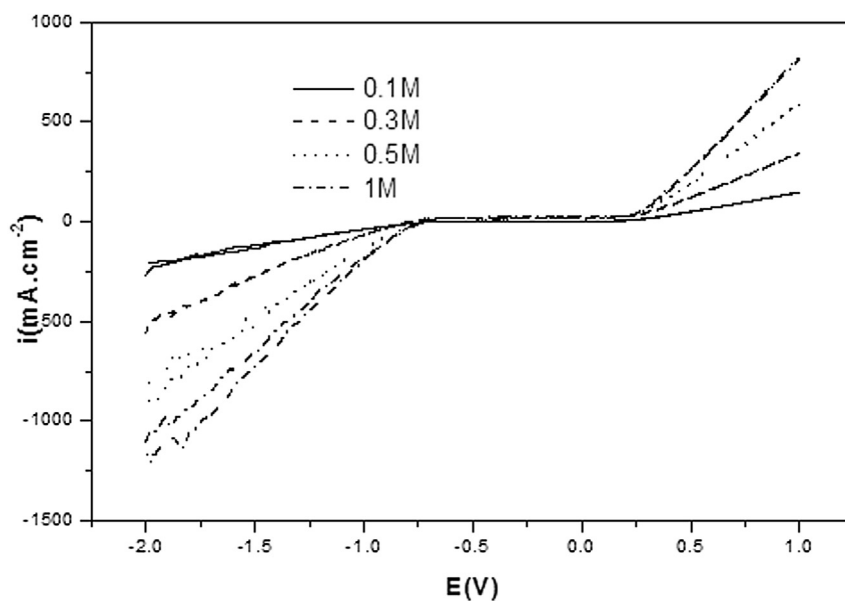


Fig. 2. Cyclic voltammograms for Mo electrode immersed in stagnant naturally aerated H₂SO₄ solution of different concentrations at 25 °C and scan rate 50 mV s⁻¹.

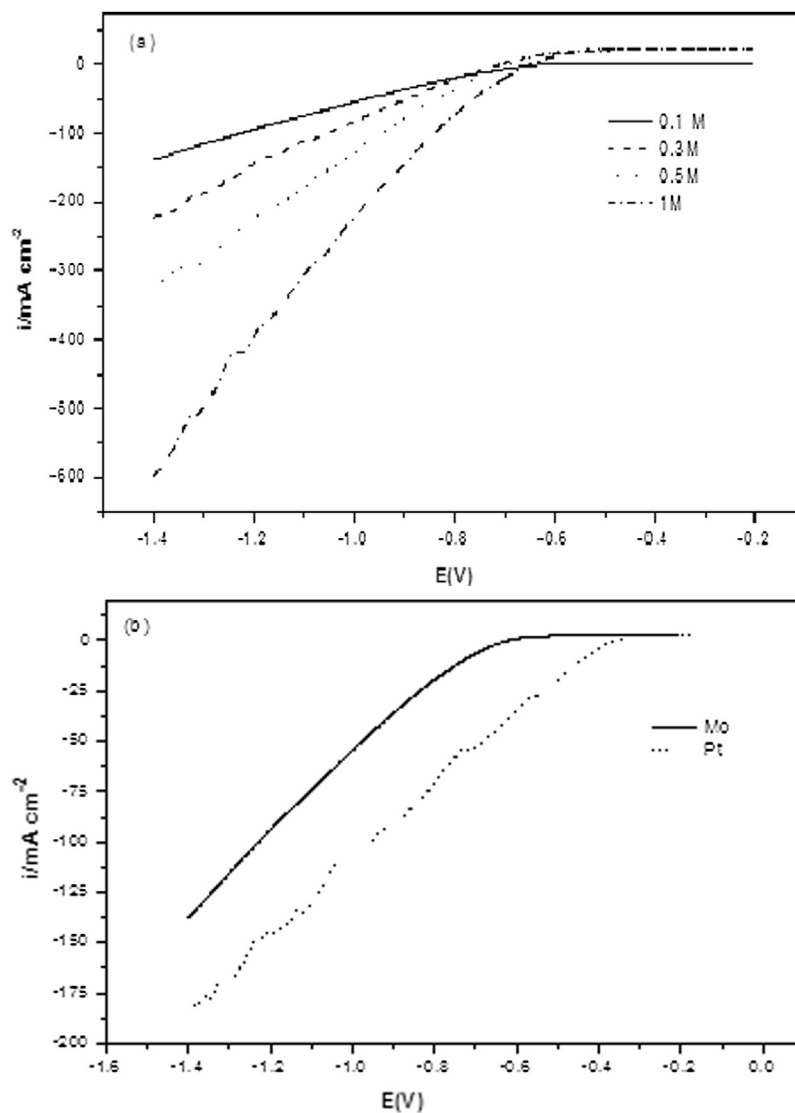


Fig. 3. a) Cathodic polarization curves for the HER on Mo electrode in solutions of different concentration of H₂SO₄ at 25 °C. b) Cathodic polarization curves for HER on Mo and Pt in 0.1 M H₂SO₄ at 25 °C.

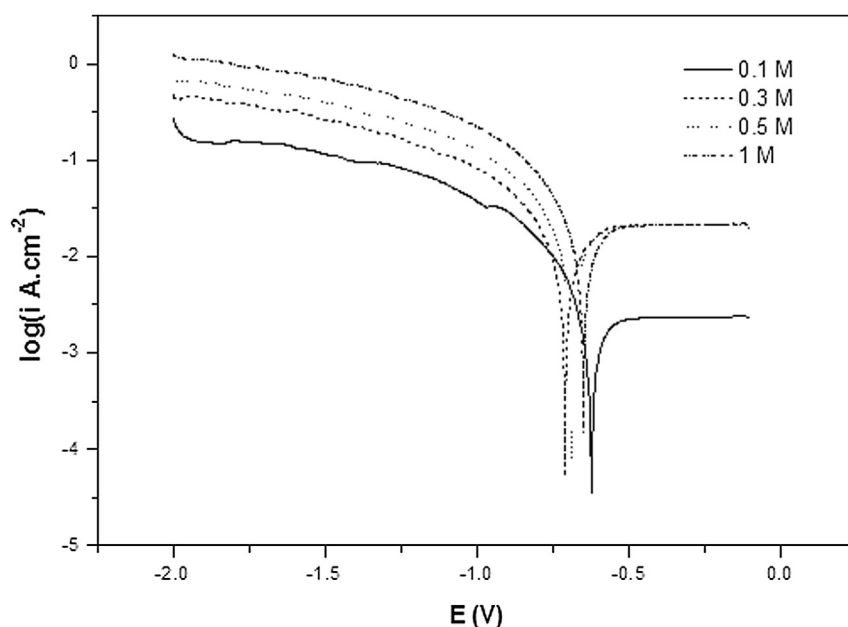


Fig. 4. Potentiodynamic polarization curve of Mo electrode after 60 min of electrode immersion in H_2SO_4 solutions of different concentrations at 25 °C.

Table 1

Potentiodynamic polarization parameters of Mo after 1 h of electrode immersion in stagnant naturally aerated H_2SO_4 solutions of different concentrations at 25 °C.

Conc. (H_2SO_4)	E_{corr} (mV)	i_{corr} (mA cm^{-2})	β_a (mV/dec)	β_c (mV/dec)
0.1 M	−604	0.9	147.2	−98.6
0.3 M	−706	3.7	128.9	−113
0.5 M	−682	4.6	129.3	−109.9
1.0 M	−647	5.1	125.1	−98.5

HER, especially on metallic surfaces. Barrier films, adsorbed layers or corrosion products play an important role in understanding the mechanism of this reaction. Electrochemical impedance spectroscopy, EIS, is a powerful technique that enables investigations at stationary conditions, where the surface morphology does not change.

Mo was used successfully to produce hydrogen from KOH solutions at a reasonable rate and for a relatively long time [14]. The disadvantages of alkaline water electrolysis are mainly related to their low efficiency and high energy consumption [24]. The use of acid electrolytes provides a potential alternative to this issue. In more aggressive acid media, platinum and some other noble metals are, till now, the best and most extensively used electro-catalysts for hydrogen evolution. This is because of the low hydrogen over-potential and the high corrosion resistance in acid media. These materials are expensive and cannot be used for hydrogen production on a large scale.

The aim of our investigation is the use of Mo metal as cathode for the HER and the large scale production of hydrogen in acidic solutions for practical applications. In this respect, steady state potential measurements, cyclic voltammetry and polarization

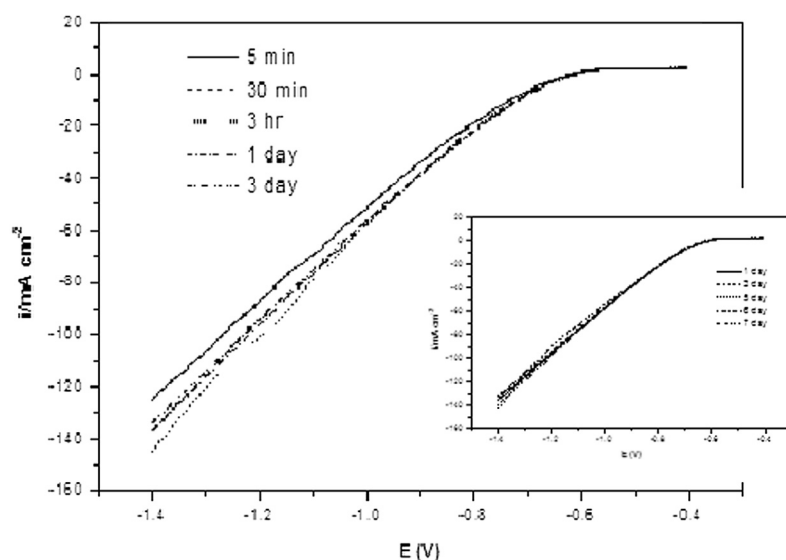


Fig. 5. Cathodic hydrogen evolution curves for Mo electrode immersed in stagnant naturally aerated 0.1 M H_2SO_4 solution after different time intervals up to 7 days at 25 °C.

Table 2

Values of the rate of hydrogen evolution on Mo after different intervals of electrode immersion in stagnant naturally aerated 0.1 M H₂SO₄ solution at 25 °C and polarization at different cathodic potentials.

Time	–0.8 V	–1 V	–1.2 V
5 min	18.6	51.2	87.2
30 min	21.0	56.1	93.7
3 h	20.8	57.7	101.1
24 h	21.8	57.4	96.2
72 h	22.1	56.6	94.6
96 h	21.1	57.2	96.3
120 h	21.4	53.9	90.2
144 h	20.7	56.9	97.8

techniques were used. Electrochemical impedance spectroscopy was also applied not only to confirm the electrochemical measurements but also to emphasize the kinetics and mechanism of the cathodic hydrogen evolution on Mo in H₂SO₄.

2. Experimental

The working electrodes were prepared from spectroscopically pure molybdenum rods (Aldrich-Chemie), mounted in glass tubes of appropriate internal diameter by an epoxy resin leaving a front surface area of 0.20 cm² to contact the electrolyte. The electrochemical cell was an all glass three electrode electrolytic cell with a large area Pt counter- and saturated calomel, SCE, reference electrodes. Before each experiment the working electrode was abraded using successive grades emery papers down to 2000 grit then washed with triple distilled water and transferred quickly to the electrolytic cell. The electrochemical measurements were carried out in aqueous solutions, where analytical grade reagents and triply distilled water were always used. The test electrolytes were freshly prepared H₂SO₄ solutions of different concentrations obtained by appropriate dilution of a concentrated acid solution. The polarization experiments and electrochemical impedance spectroscopic investigations, EIS, were performed using a Voltalab PGZ 100 “All in

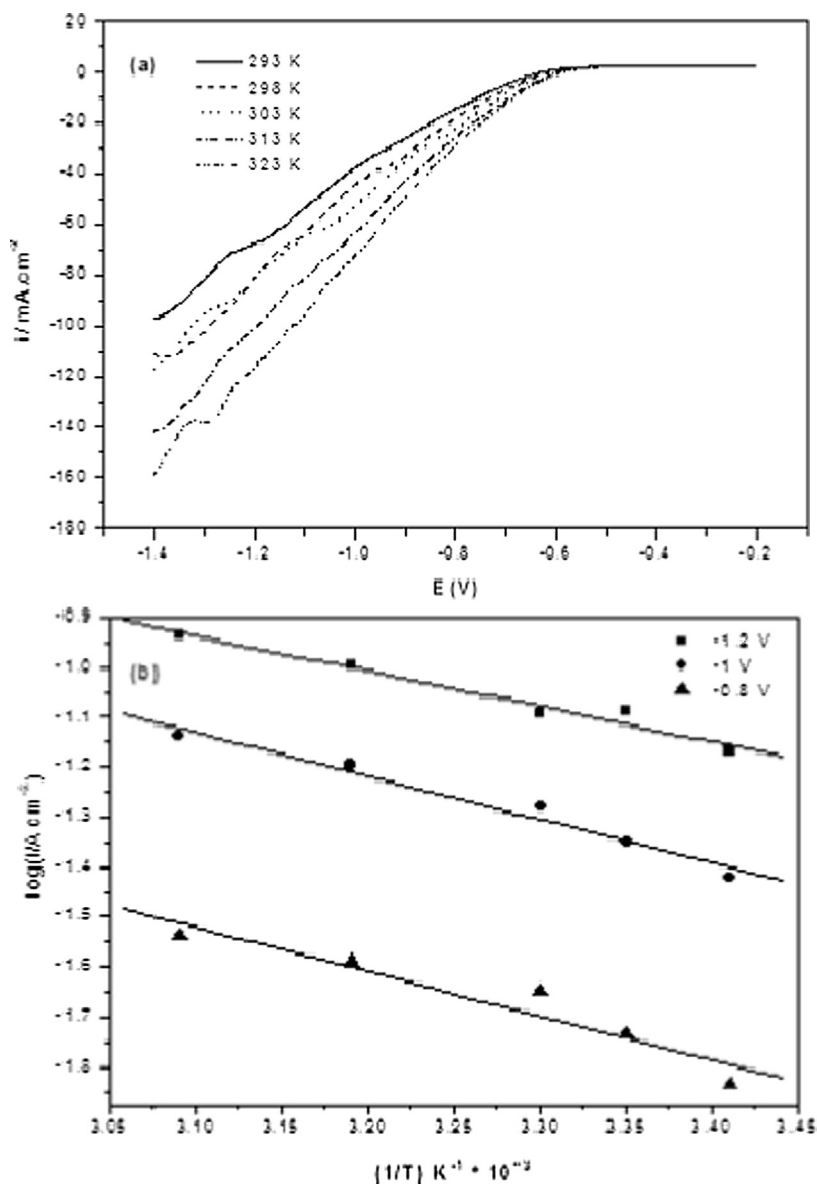


Fig. 6. a) Cathodic hydrogen evolution on Mo electrode at different temperatures in stagnant naturally aerated 0.1 M H₂SO₄ solution. b) Arrhenius plots for the cathodic hydrogen evolution on Mo electrode at different temperatures and different polarization potentials.

one” potentiostat/galvanostat system. The potentials were measured against and referred to the saturated calomel reference, SCE, (0.245 V vs. the standard hydrogen electrode, SHE). All potentiodynamic polarization experiments were carried out using a scan rate of 5 mV s^{-1} to achieve quasi-stationary conditions. The impedance, Z , and phase shift, θ , were recorded in the frequency domain $0.1\text{--}10^5 \text{ Hz}$. The superimposed ac-signal was 10 mV peak to peak. To achieve reproducibility, each experiment was carried out at least twice. Details of experimental procedures are as described elsewhere [14,25].

3. Results and discussion

In the following sections, the general electrochemical behavior of molybdenum in H_2SO_4 solutions of different concentrations was investigated. The cathodic hydrogen evolution reaction on Mo under different conditions was studied and a comparison of the recorded rate of hydrogen evolution on Mo with that on Pt electrode under the same conditions was carried out.

3.1. Open circuit potential measurement

The open circuit potential of Mo electrode was traced over 1 h in stagnant naturally aerated H_2SO_4 solutions of different concentrations. The results of these experiments are presented in Fig. 1a. At all concentrations the steady state is reached within $\approx 20 \text{ min}$ from the electrode immersion in the acid solution. At the moment of electrode immersion, a large increase was recorded, and then a gradual increase of potential with time is taking place until a steady state is reached. The electrode potential gets more positive with time indicating a natural tendency of Mo for passivation in aqueous solutions even when aggressive acid solution is used. There is no appreciable change in the steady state potential by increasing the concentration of H_2SO_4 . This indicates that the dynamic equilibrium between film formation and film dissolution is not affected by the acid concentration. For comparison, the variation of the open circuit potential of Pt in H_2SO_4 solution was also traced and the results of both Pt and Mo are presented in Fig. 1b. The remarkably negative steady state potential of Mo suggests that the HER on this metal may take place at relatively lower overpotential.

3.2. Cyclic voltammetry measurements

The cyclic voltammograms of the Mo electrode recorded at a scan rate of 50 mV s^{-1} in H_2SO_4 solution of different concentrations at 25°C are presented in Fig. 2. The scan was started at -2 V where hydrogen was clearly evolved at the electrode surface. The direction of the scan is shown on a typical cyclic voltammogram for the 0.1 M acid concentration as inset in Fig. 2. All measurements were carried out in the same way. In the potential range from -650 to $+300 \text{ mV}$ a transition region was recorded, where the current density stabilizes with potential. This transition region is attributed to the formation of MoO_2 . In this potential range the film formed on Mo consists mainly of MoO_2 as revealed from XPS analyses in $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. At higher anodic potentials Mo[V] and Mo[VI] oxides may be formed and Mo[IV] oxide represents the main ratio [26,27]. At more positive potential a pronounced increase of the current was recorded, which is attributed to O_2 evolution.

3.3. Potentiodynamic polarization measurements

3.3.1. Effect of concentration

To obtain more information about the effect of sulfuric acid on the HER, cathodic polarization curves of Mo electrode were

recorded at different concentrations of sulfuric acid to -1.4 V , where the cathodic hydrogen evolution was taking place at an appreciable rate. Fig. 3a shows a set of such polarization curves. It is clear that the rate of hydrogen evolution increases by increasing the concentration of H_2SO_4 . The increase of concentration of H_2SO_4 from 0.1 to 1.0 M has increased the current density corresponding to the HER from 18 to 72 mA cm^{-2} at -0.8 V and from 82 to 395 mA cm^{-2} at -1.2 V .

For comparison the steady-state polarization curves of Mo and Pt in $0.1 \text{ M H}_2\text{SO}_4$ solution are presented in Fig. 3b. It is clear that the current density corresponding to the HER on Pt in the same solution is larger than that recorded on Mo. The steady state potentials of Pt and Mo are 439 and -11 mV , respectively, (cf. Fig. 1b). The potential at which hydrogen starts to evolve in the same solution on the two different metals is -360 and -620 mV for Pt and Mo, respectively (cf. Fig. 3b). According to the recorded values, the overpotential for hydrogen evolution on Mo amounts to -609 mV whereas that on Pt is -799 mV . This means that Mo is a promising cathode for hydrogen evolution in H_2SO_4 solutions. To compare between Mo and Pt from the point of view of the rate of hydrogen evolution under the same polarization conditions we can conclude that Mo is not only comparable but also better than Pt. The current density corresponding to the HER on Mo at -1.0 V from the steady state potential amounts to 46.2 mA cm^{-2} whereas that on Pt under the same conditions amounts to 28.5 mA cm^{-2} . The presented data were extracted from Fig. 3b at a concentration of $0.1 \text{ M H}_2\text{SO}_4$ only. At higher concentration the rate of hydrogen evolution on Mo will be higher (cf. Fig. 3a).

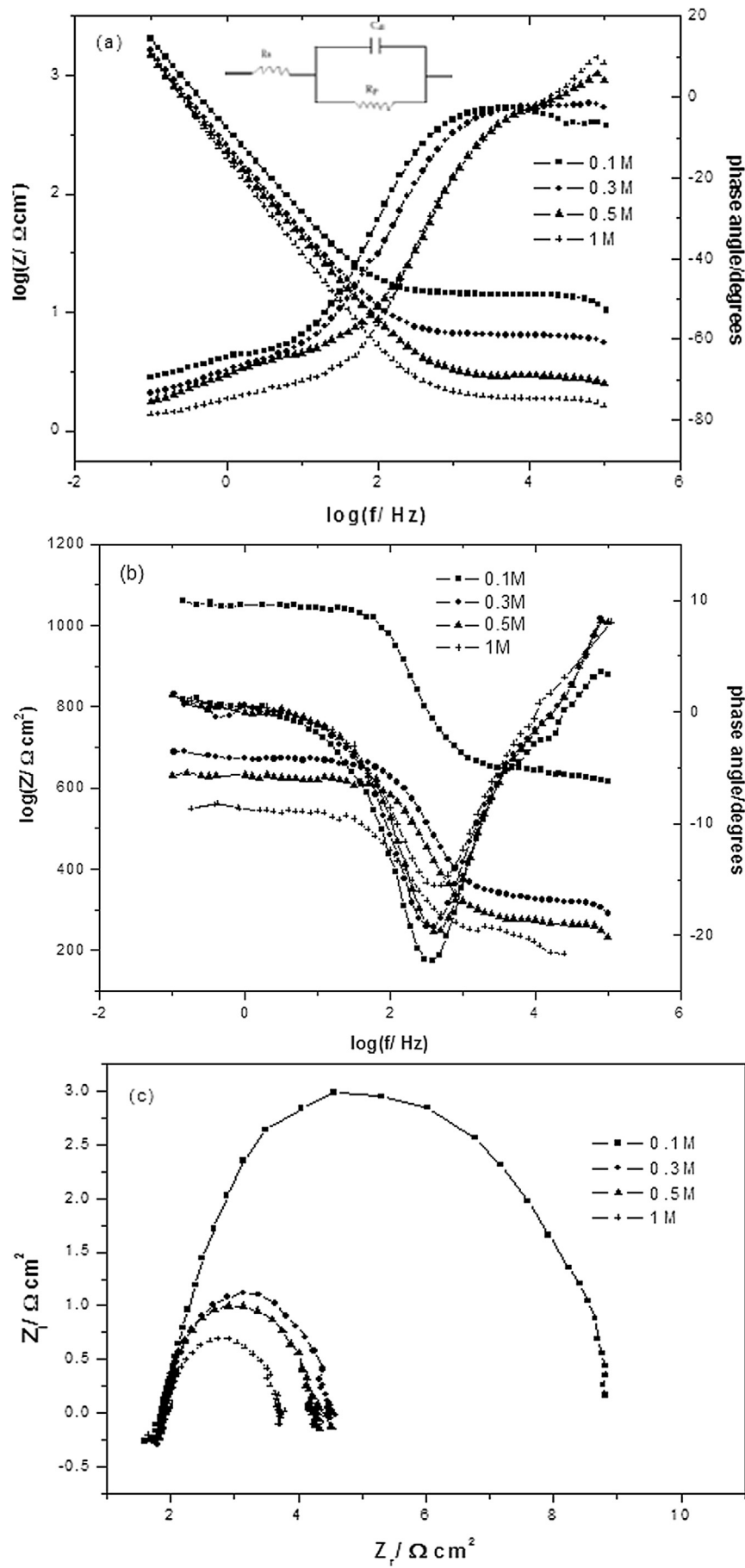
The corrosion characteristics of the Mo electrode in sulfuric acid solutions with different concentrations were investigated by using the Tafel extrapolation technique. The measurements were carried out at a scan rate of 5 mV s^{-1} after holding the electrode at the open-circuit potential for 60 min in stagnant naturally aerated H_2SO_4 solutions of different concentrations. The recorded data are presented in Fig. 4. The values of the corrosion parameters i.e. corrosion potential, E_{corr} , corrosion current density, i_{corr} , corrosion rate and the Tafel slopes β_a & β_c , were calculated and presented in Table 1. It is worthwhile to mention that the recorded corrosion potential is more negative than the steady state potential by about 650 mV . This difference can be attributed to surface activation due to the prior cathodic polarization and the removal of the native passive film [27–29]. At the starting potential of -1.4 V , a relatively high current density corresponding to the HER was recorded. This current density is affected by the acid concentration as presented in Fig. 3a. The value of the anodic Tafel slope, β_a , is in the range of 120 mV , which suggests a two electron transfer process for the metal dissolution:



and the formed Mo^{2+} oxidizes to give the passive MoO_2 film even in acidic media.

3.3.2. Effect of immersion time on HER

In our investigations we have used the electrode continuously for 7 days in $0.1 \text{ M H}_2\text{SO}_4$ and no poisoning effects or deterioration of the rate of hydrogen evolution was recorded. The cathodic hydrogen evolution curves recorded on Mo in $0.1 \text{ M H}_2\text{SO}_4$ solution after different time intervals of electrode immersion are presented in Fig. 5. The values of the rate of hydrogen evolution on Mo at different polarization potentials in stagnant, naturally aerated $0.1 \text{ M H}_2\text{SO}_4$ solution at 25°C and different time intervals were calculated and presented in Table 2. It is easy to notice that the rate of hydrogen evolution at any polarization potential from the



beginning up to 7 days is approximately the same (the current density on Mo electrode varies in a very narrow range). It means that the Mo electrode can be used for hydrogen production conveniently without any pronounced change in the rate of the HER and any special treatment.

3.3.3. Effect of temperature on the rate of HER

The effect of temperature on the rate of hydrogen evolution on the Mo electrode in naturally aerated stagnant 0.1 M H₂SO₄ solution was investigated. The variation of the cathodic current density with temperature is presented in Fig. 6a. Generally and as it is expected, the rate of hydrogen evolution increases as the temperature increase. The rate of hydrogen evolution is proportional to the corresponding current density, i_c , recorded at a specified potential. The values of current density at –0.8, –1.0 and –1.2 V were extrapolated at different temperatures and the corresponding results were plotted and presented in Fig. 6b. The activation energy of the hydrogen evolution process was calculated for each polarization potential according to the familiar Arrhenius equation [30]. The calculated value of E_a was found to decrease with increasing the polarization potential, which means that the hydrogen evolution is taking place easier at more cathodic potentials. The calculated values were 17.04, 16.36 and 13.5 kJ mol^{–1} at –0.8, –1.0 and –1.2 V, respectively. The low activation energy of the hydrogen evolution process indicates the ease of hydrogen evolution on Mo in H₂SO₄ solution and supports that the HER is controlled by a single electron transfer step [31,32].

3.4. Electrochemical impedance spectroscopic investigations, EIS

EIS is a powerful tool for studying corrosion phenomena, especially when passive films are considered. An important advantage of this technique is the use of a small ac signal without significantly disturbing the electrode surface morphology or the properties being recorded. Also, it is possible to simulate the experimental impedance results to pure electronic models that can verify or rule out mechanistic models and enable the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system [33–38]. The electrochemical behavior of Mo was investigated after 1 h immersion in stagnant, naturally aerated H₂SO₄ solution of different concentrations by EIS. The recorded experimental results are presented as Bode plots in Fig. 7a. The Bode format enables equal presentation of all impedance data and the phase angle, θ , as a sensitive parameter for interfacial phenomena, appears explicitly [33]. The general behavior of Mo is the decrease of total impedance, Z , with increase of H₂SO₄ concentration. This means that the charge transfer resistance of the electrode process decreases as the concentration of sulfuric acid increases.

Since the EIS is a nondestructive technique and the measurements at any polarization potential describe the reaction occurring at the electrode/electrolyte interface without any disturbance of the electrode surface, it was important to investigate the impedance behavior of the Mo electrode during hydrogen evolution. Fig. 7b presents the Bode plots of cathodically polarized Mo electrode at –750 mV in stagnant, naturally aerated H₂SO₄ solutions of different concentrations, where the HER is taking place at an appreciable rate. The experimental impedance data were fitted to theoretical data according the equivalent circuit model presented

Table 3

Equivalent circuit parameters for Mo recorded after 1 h of electrode immersion in stagnant naturally aerated H₂SO₄ solution of different concentration under –750 mV cathodic polarizations at 25 °C.

Conc. of H ₂ SO ₄	R_s (Ω)	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ^{–2})	α
0.1 M	4.32	7.02	226.5	0.892
0.3 M	2.08	2.64	241.0	0.823
0.5 M	1.89	2.43	263.3	0.909
1.0 M	1.72	1.81	175.5	0.903

in Fig. 7a (inset). The data were analyzed using software provided with the impedance system, where dispersion formula for such simple equivalent circuit model was used. The model consists of a resistor, R_s , representing the solution resistance in series with a parallel combination consisting of a resistor representing the charge transfer resistance, R_{ct} , and a capacitor, C_{dl} , representing the double layer capacitance. For such combination the total impedance, Z , is given by:

$$Z = R_s + [R_{ct} / \{1 + (2\pi f R_{ct} C_{dl})^\alpha\}] \quad (2)$$

where α denotes an empirical parameter ($0 \leq \alpha \leq 1$) and f is the frequency in Hz [33,34]. The calculated fitting impedance parameters after different intervals of hydrogen evolution are summarized in Table 3. The results of these experiments show that the general behavior of the metal is the same whatever the time of application of the electrode. The electrode resistance has low value; this can be attributed to the surface activation of the Mo electrode due to the HER. The phase angle, θ , shifts toward higher values and the impedance, Z , decreases as the acid concentration increases indicating an increase in the rate of hydrogen evolution. Under cathodic polarization no broadening of $\log f$ vs θ curve was recorded, even in dilute acid solution, which means that the rate of hydrogen evolution is high. It is important to mention that the calculated value of α at all investigated acid concentrations approaches unity which means that the electrode/electrolyte interface behaves like an ideal capacitor and therefore the use of a constant phase element to describe the electrode/electrolyte interface instead of the capacitor is not necessary [28,33].

4. Conclusions

Molybdenum can be considered as a promising cathode for the hydrogen evolution reaction in acidic solutions. Polarization and impedance results have shown that Mo is even better than Pt, not only in dilute (0.1 M H₂SO₄ solution) but also in concentrated (≥ 1.0 M) acid solutions. The electrode can be used continuously for at least 7 days without any deterioration or decrease in the rate of the hydrogen evolution. Prolonged hydrogen evolution leads to electrode activation due to the reduction of native passive film and an increased rate of hydrogen evolution can be recorded. The activation energy of the HER is low [≈ 13.5 kJ mol^{–1} at –1.2 V in 0.1 M H₂SO₄ solutions] and the hydrogen evolution process is controlled by single electron transfer step.

Fig. 7. a) Bode plots for Mo electrode immersed in H₂SO₄ solutions of different concentrations after 60 min of electrode immersion at 25 °C. a) (inset): Equivalent circuit model used in the impedance data fitting. Where R_s = solution resistance, R_p = polarization resistance, C_{dl} = double layer capacitance. b) Bode plots for Mo electrode at $E = -750$ mV vs SCE, for HER at different concentrations of H₂SO₄ solutions at 25 °C. c) Nyquist plots for Mo electrode at $E = -750$ mV vs SCE, for HER at different concentrations of H₂SO₄ solutions at 25 °C.

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